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The DADI model: Computation of the mass absorption cross section of two coalesced soot nanoparticles from atomistic information

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1 Introduction

Soot particles emitted by combustion processes are suspected to have a non-negligible impact on the Earth's radiative balance, as well as on the health of people exposed to these particles [1, 2, 3]. Moreover, many carbonaceous compounds of various sizes have been detected in our Galaxy, ranging from polycyclic aromatic molecules (PAHs) to fullerenes and soot-like grains [4]. In these astrophysical environment, carbonaceous dust are suspected to play a crucial role in the physics and the chemistry of the medium [5].

Up to now, remote observation of the interaction of this carbonaceous systems with light is the only way of deciphering their structure, in situ. Thus, we seek to get better estimations of the absorption cross sections of these particles in the UV-visible part of the spectrum as a function of the geometric and chemical details of their structure, to better characterize them.

Among the methods used to compute the optical properties of particles with arbitrary shapes, the Dynamic Atomic Dipole Interaction (DADI) model – developed in Besançon [6, 7, 8,

9] and implemented in the (home-made, non public) `polar_scatt` code – is similar to the classical Discrete Dipole Approximation (DDA) [10, 11, 12], but has the distinctive advantage of being sensitive both to the atomistic geometry of the particles and to the chemical functions it contains. This model, however, requires an adequate parametrization of the atomic, frequency-dependent polarizabilities for all the atomic species forming the particles, over the UV-visible spectrum, as well as the knowledge of the atomic coordinates of all the atoms in the particle.

The first applications of our DADI-model were focused on the calculation of the mass absorption cross section of various isolated nanoscale spherules, entirely made of carbon atoms, aiming at modeling 'building blocks' of soot particles, composed of several of those spherules, and characterized by a fractal dimension [6, 7, 8, 9]. In these works, various internal geometries of the nanoparticles were modeled at the atomic scale, i.e., by defining explicitly all the atomic positions, using a home-made procedure [13, 14]. The other ingredient, that is the frequency-dependent polarizabilities of the carbon atoms were taken either from experimental data available for graphite[15] or, more recently, from the results of high-level DFT calculations performed on fullerenes [9].

In real situations however, soot nanoparticles usually form aggregates soon after their emission [16], and it has been proven that the resulting overlapping of these elementary nanoparticles may influence their optical properties [17].

Thus, here we have used the DADI-model to simulate the UV-Visible spectrum of two coalesced soot particles of nanometer sizes. This has been done by modeling, at the atomic scale, two identical carbonaceous spherules made of 2753 carbon atoms, and by varying the distance between their geometrical centers, up to a given degree of interpenetration.

2 Methods

2.1 The DADI model

The DADI model is inspired both by the Discrete Dipole Approximation (DDA) [10] and the Point Dipole Interaction (PDI) [18] approaches, because it uses classical equations of DDA, but with cartesian coordinates (\vec{r}_i) and (frequency-dependent) polarizability tensor $\bar{\bar{\alpha}}_i(\omega)$ for each of the N atoms ($i = 1..N$) of the system under consideration (here, soot nanoparticles), as in PDI, instead of positions on a discretized cartesian grid and effective polarizabilities calculated from macroscopic dielectric permittivities, as in DDA.

Indeed, we can compute the dipole on atom i $\vec{\mu}_i(\omega)$ as the sum of a contribution induced by the incident field $\vec{E}_0(\omega)$ applied to the nanoparticle and of the contributions coming from all the dipoles induced on the N atoms (allowing the possibility of a self-interaction since a real atom is not point-like):

$$\vec{\mu}_i(\omega) = \bar{\bar{\alpha}}_i(\omega)\vec{E}_0(\vec{r}_i, \omega) + \sum_{j=1}^N \bar{\bar{\alpha}}_i(\omega)\bar{\bar{T}}(\vec{r}_i, \vec{r}_j, \omega)\vec{\mu}_j(\omega). \quad (2.1)$$

where $\bar{\bar{T}}$ is the electric field interaction tensor, including retardation effects ($\bar{\bar{T}}(\vec{r}_i, \vec{r}_j, \omega)$ is $-A_{i,j}$ of e.g.[11])

Collecting Eq. 2.1 for the N values of index i , we get a $3N \times 3N$ dense matrix system whose resolution, for a given incident field, gives a $3N$ vector that contains the N dipoles $\vec{\mu}_i(\omega)$ located on each atom. In the DADI model, once the atomic dipoles are self-consistently computed, their values are used to calculate various optical properties of interest, such as the extinction, diffusion and absorption cross sections, Mueller matrix and asymmetries, as in DDA [11]. Note that, because the atomic positions are not on a regular grid, we cannot use the usual FFT tricks implemented in DDA[12].

2.2 Model of the two coalesced soot particles

To model two, more or less interpenetrated soot nanoparticles at an atomistic level, we built two identical carbonaceous spherules using our home-made procedure [14]. Each nanoparticle has thus an onion-like structure made of four carbon layers arranged in a concentric way, in which a few carbon atoms have been randomly removed to mimick the defective nature of soot. Each particles thus contains a total of 2753 carbon atoms and has an external radius of about 35 Å. Its structure has been optimized with the molecular dynamics software LAMMPS [19] and using the AIREBO interaction potential between carbon atoms [20], to get the atomic coordinates of the particles in a stable configuration.

Then, the interpenetration process has been simulated with LAMMPS by initially placing the two nanoparticles close together, with a minimum distance of 5 Å between their external layers, and progressively decreasing, in a step-by-step process, the distance between them. The equilibrated atomic coordinates obtained after a minimization and an equilibration computation at 5 K has been dumped for each step of the interpenetration process (see Figure 1).

3 Results

The mass absorption cross sections for the two soot nanoparticles described above have been calculated using the DADI model, as a function of the incident energy and for different distances between these two particles . In these calculations, the atomic coordinates have been taken from the results of the MD simulations.

An analysis of these MD results, performed with a Python code coming from Ref. [16], indicates that the ratio between the numbers of aromatic-like and aliphatic-like carbon atoms in the particles decreases by 18 % between the first (separated nanoparticles) and the last (interpenetrated nanoparticles) situations. Note that aromatic-like carbons are defined as those

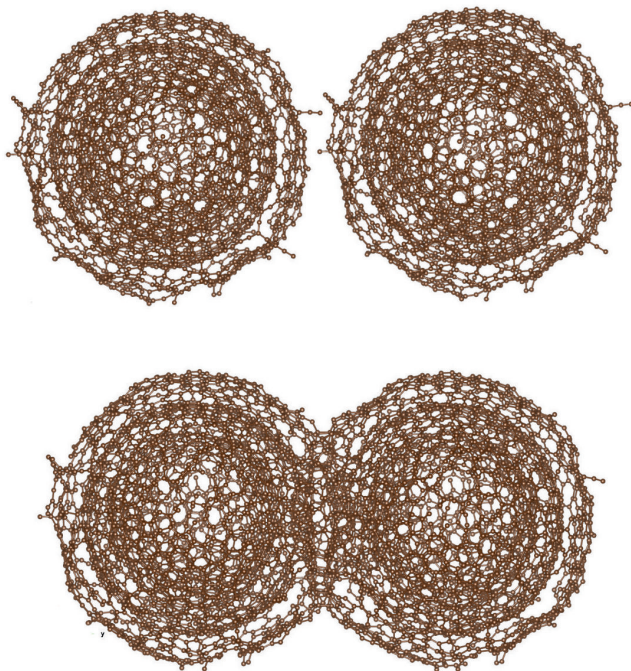


Figure 1: Relaxed structures of two soot nanoparticles made of 2753 carbon atoms each, located at different distances from each other (separated (left hand side of the Figure) and interpenetrated (right)).

which are bound to three other carbons. All the carbon atoms which are in a different configuration are considered as being aliphatic-like. Anyway, this indicates that different types of carbon atoms are present in the soot nanoparticles, and that it is mandatory to consider different atomic polarizabilities in the DADI model. As in our previous works [6, 7, 8], the values of these atomic polarizabilities have been calculated using parameters given by Draine for graphite [15]. More precisely, the aromatic-like carbon atoms have thus been characterized by anisotropic polarizability tensors, while isotropic polarizabilities have been considered for the aliphatic-like carbons [8].

The results of the calculations performed with the DADI model are given on Figure 2, for various distances (5 \AA , 0 \AA , and -5 \AA) between their external layers.

As can be seen, the interpenetration of the two soot nanoparticles results in a shift in position and amplitude of the two absorption peaks. This can be directly attributed to the change in the ratio of aromatic-like over aliphatic-like carbon atoms and related to the different polarizability values that have been considered for these types of atoms. Note that if we look especially at the position of the first peak, a 5 nm redshift is evidenced upon coalescence of the particles. Such a shift in the absorption spectrum might be experimentally measured because the resolution of UV-visible spectrometer is around a tenth of nanometer [21].

4 Conclusion

Here, by using the DADI model, we have shown that the decrease of the aromatic-like over aliphatic-like carbon atoms ratio in the coalesced particles results in redshifts of the maxima of the peaks in the mass absorption cross section spectrum that could be experimentally measured. These shifts increase with the degree of interpenetration, because of polarizability change on the carbons. Of course, a more precise evaluation of these shifts could be achieved by having polarizability values more relevant to soot nanoparticles than those coming from graphite

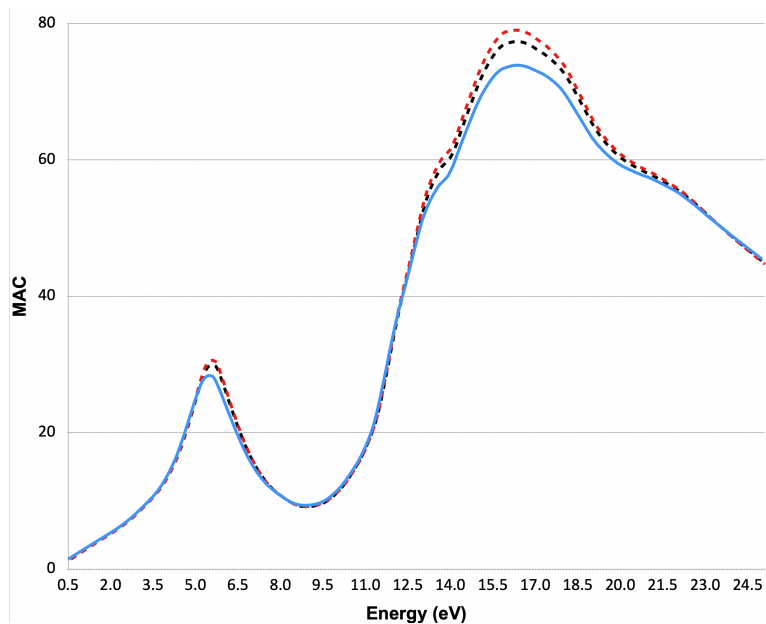


Figure 2: Mass absorption cross section (in m^2/g) for the two soot nanoparticles considered in the present study, calculated with the DADI model, as a function of the energy and at three different typical distances (separated (red, dashed), touching (black, dashed) interpenetrated (blue, solid line) particles).

data. This work, initiated recently in our group on the basis of high-level DFT calculations [9], is still in progress.

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